ENVIRONMENTAL PROTECTION

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WASTELESS TECHNOLOGY FOR PRODUCTION OF FIBERGLASS LAMINATE BASED ON ALUMINOPHOSPHATE BINDER

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Technology for production of glass laminate based on aluminophosphate binder involving pressure molding of previously dried glass fabric pieces with a deposited suspension of the powder filler in the binder (prepreg) allows for a considerable decrease in consumption of the initial components and significantly improves the mechanical strength of the material. The possibility of using crushed clippings and chips of glass laminate as a powder filler is demonstrated.

Glass laminates based on inorganic phosphate binders differ from glass laminates based on organic and organosilicon polymer binders by their incombustibility and ability to retain relatively good physicomechanical parameters under the long-term effect of high temperatures. Their good electrophysical properties, such as volume resistivity of up to $10^{14}\ \Omega \cdot cm$ at normal temeperature and at least $10^{6}\ \Omega \cdot cm$ at 1000°C, low dielectric constant (~ 3.5) and a low dieletric loss tangent ($\sim 5 \times 10^{-2}$), which vary insignificantly at high temeperatures, were the reason for the use of glass laminates based on phosphate binders as high-temeperature electrical insulating and radio transmitting materials in missile and aerospace engineering (RF Pat. Appl. 93008111/133/007304 with priority of 01/04/96, RF patent RU 2076086 C1) [1] and in electrical equipment for steel production [2, 3]. The incombustibility and absence of poisonous volatile emissions at high temperatures made it possible to recommend the glass laminate as a fireproof material for production and interior decoration of transport vehicles, in particular, subway cars [4, 5].

TABLE 1

Initial suspension	Suspension density, g/ml		Content of α-Al_2O_3 powder filler in suspension, wt. %	
	initial	released	initial	released
1	2.223	2.153	54.3	45.8
2	2.252	2.070	55.9	43.9
3	2.253	2.170	54.1	50.0

The process of glass laminate production consists of the following phases:

preparation of the binder in the form of a viscous aqueous solution of metal phosphates of aluminum, chromium, magnesium, and other metals;

preparation of suspensions of the powder filler (oxides of chromium, aluminum, etc.) in the binder;

impregnation of fiberglass fabric or tape with organosilicon lacquer and subsequent drying, in order to protect the glass fiber from being corroded by the acid (pH ~ 1.0) binder in heat treatment;

deposition of the suspension on the glass fabric pieces for obtaining laminates of the required thickness, or on the fiberglass tape for subsequent wrapping of the tape on a mandrel;

heat treatment under pressure using a press or an autoclave;

manufacture of pieces of the required shape and dimensions by machine treatment employing hard-alloy tools.

The main waste products of the process include the suspension squeezed out in heat treatment under pressure and chips arising in machine treatment. Wasteless technology was tested in the production of fiberglass laminate based on KT-11-TO silica glass fabric impregnated with a solution of KM-9K organosilicon resin, aluminophosphate binder with a molar ratio of $P_2O_5 : Al_2O_3 = 3$, and α-Al_2O_3 powder filler with a grain size of up to 20 μm (RF Pat. Appl. 93008111/133/007304 with priority of 01/04/96, RF patent RU 2076086 C1). The glass laminate samples were heat-treated at the pressure of 1 MPa and the temperature of 270°C, with holding for 10 – 12 min per 1 mm of thickness.

TABLE 2

Initial suspension	Composition of suspension	Properties of glass laminate*: density, g/cm^3	Strength, MPa: in compression parallel to the glass fabric layers	in compression perpendicular to the glass fabric layers	bending	Specific impact viscosity, 10^{-4} J/m^2
1	100% initial suspension	1.91	33.6	178.6	66.0	5.54
1	100% released suspension	1.80	50.5	227.1	62.4	7.37
1	Initial and released suspension in the ratio 1 : 1	1.83	45.1	166.8	66.0	5.08
2	100% initial suspension	1.87	45.9	199.2	58.2	4.10
2	Initial and released suspension in the ratio 1 : 1	1.89	47.4	198.2	65.4	4.91

* The parameters were determined according to GOST 4651–82, GOST 4647–80, and GOST 4648–71.

Long production experience has established that the loss of suspension squeezed out in heat treatment reaches 50% of the amount initially deposited on the glass fabric. The highest amount of suspension escapes in the first minutes of pressure application and continues up to the temperature of 100 – 120°C. Table 1 shows that the removed suspension contains less powder filler and, accordingly, has a lower density than the initial suspension. Moreover, microscopic analysis showed that the effluent suspension contains a more highly disperse fraction of the powder filler. The higher content of the binder and the highly disperse fraction of the filler result from the effect of filtration of the suspension squeezed from the intermediate product.

The binder parameters (the ratio of P_2O_5; Al_2O_3, the amount of free and bound H_3PO_4) in the initial and effluent suspension did not differ. For recycling, a filler in the form of α-Al_2O_3 powder was added to the released suspension until the density of the initial suspension was reached. Table 2 presents the properties of the glass laminate produced using the released suspension. The data in Table 2 support the expediency of such utilization. The higher strength of the laminate made with the released suspension is probably related to the higher content of the highly disperse fraction of the filler.

In the course of machine treatment, 10 to 70% of the preform product is lost in chips and clippings. The clippings in their natural state are hard to crush, since the glass laminate has a high impact strength (specific viscosity no less than 4.5×10^4 J/m^2). After heat treatment at 600°C for several minutes, the glass laminate becomes brittle, and the shreds can be easily crushed in a ball mill. The chips recovered on machine treatment do not require any grinding before recycling. Table 3 gives the properties of the glass laminate based on crushed waste used as a powder filler.

In order to prevent squeezing of the suspension, a procedure for production of glass laminate using a prepreg (i.e., an intermediate product in the form of dried glass fabric with a deposited binder) was developed. In our case, the prepreg was glass fabric with deposited suspension, dried to remove part of the water. It was established that in preparation of the prepreg, glass fabric with the deposited suspension can be dried either spread out in air, or at a temeperature of 100 – 120°C. In drying the fabric in air at 18 – 20°C, on average 45% of the water contained in the suspension is removed in 8 h, 52% is removed in 24 h, and after that, the moisture content in the pregreg varies insignifiantly (within the limits of 1 – 2%). The prepreg obtained in this way does not stick to the hands and retains its elasticity. If the prepreg is dried at 50 – 60°C, about 67% of the moisture contained in suspension is removed in one shift (~ 6 h), and up to 80% moisture is removed in one shift at 100 – 120°C. The prepregs dried at temperatures up to 120°C preserve a sufficient degree of technological elasticity and have low (not more that 3 – 10%) moisture absorption from air in storage in factory premises (for 6 days).

When glass laminate sheets made of prepregs were heat-treated under pressure, no suspension was squeezed out even at a pressure of 5 MPa. In the case of the standard procedure, the suspension is almost totally forced out in heat treatment at a pressure above 2.4 MPa, and it is impossible to obtain a laminate of satisfactory quality: the resulting laminate is too "dry" and easily flakes in machine treatment.

TABLE 3

Content of crushed clippings in the filling powder, %	Strength of glass laminate*, MPa: in compression parallel to the glass fabric layers	in compression perpendicular to the glass fabric layers	bending	Specific impact strength, 10^{-4} J/m^2
Without clippings	70.4	284.0	72.0	4.05
20	73.9	233.3	66.0	4.80

* The plates were made using a prepreg.

TABLE 4

Specific molding pressure, MPa	Density of glass laminate, g/cm^3	Strength, MPa in compression parallel to the glass fabric layers	in compression perpendicular to the glass fabric layers	bending	Specific impact strength, 10^{-4} J/m^2
		Standard techology			
1.0	1.91	33.6	178.6	66.0	5.54
		Proposed technology			
0.5	1.83	45.9	244.0	49.2	4.12
2.5	–	57.0	243.0	49.2	3.99
5.0	2.33	94.6	303.0	54.0	3.75
		After storing the prepreg for 32 days			
1.0	–	36.0	196.6	69.6	3.52

A laminate of satisfactory quality is obtained from prepreg dried at the temperature of 200°C, when nearly all moisture is removed (up to 94% of the water contained in the suspension). This points to the existence of thermoplastic properties in the aluminophosphate binder dried at temperatures below 200°C. The prepreg dried at the temeperature of 200°C is stiff and technologically unsuitable.

The glass laminate obtained from the prepreg has significantly higher strength patameters than the laminate produced according to the standard "wet" technology. The slight increase in the duration of the production process caused by the need for drying of the prepreg is fully compensated, since losses of suspension under pressure are excluded and the properties of the laminate improve. The data in Table 4 indicate the possibility of prolonged storage of the prepreg. The higher strength of the glass laminate made of prepreg is due to the higher matrix density. The matrix of the laminate produced by the standard technology contains three times more pores than the laminate made of prepreg, moreover, the latter has no large pores at all. In addition, the proposed technology makes it possible to apply a higher molding pressure, which can significantly increase the strength of the glass laminate.

The calculations showed that the cost of production of glass laminate made of prepreg is below the cost of traditional laminate. This is due to the lower quantity of the glass fabric and, accordingly, the suspension, required for production of 1 kg of glass laminate, since the suspension is not squeezed in pressing, and an intermediate layer of matrix appears between the glass fabric layers. In the laminate produced by the standard technology, the matrix is only located between the glass fibers and in the voids of the fabric, owing to the removal of the suspension under pressure.

Thus, the use of the wasteless technology makes it possible to protect the environment and to lower the production cost.

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